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A COMMENTARY ON SOLID LUBRICANTS AND WEAR-RESISTANT SOLIDS FOR USE IN EXTREME ENVIRONMENTS

Harold E. Sliney

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

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INTRODUCTION

This paper introduced the first half of a two-session symposium on the subject of Lubricants for Extreme Environments. The first session addressed the subjects of solid lubrication and wear-resistant solids. The topics of this session were diverse and included discussions of 1) the recent progress in the solid lubrication of rolling-element bearings; 2) the status of polyimide-based solid lubricating materials; 3) plasma physics techniques for coating and surface modification; and 4) the potential ultimate in high-temperature rolling-element bearings - the ceramic bearing.

High temperatures are usually associated with extreme environments, but the chemical reactivity of the atmosphere is equally relevant. Obviously many lubricant materials can be used at much higher temperatures in inert atmospheres than in an oxidizing air atmosphere. High loads and velocities are also contributary and in fact all of these factors are interactive in determining the overall severity of the application.

It is interesting to consider some examples of why high-temperature solid lubrication is of interest for today's technology. The space shuttle is the most highly publicized example of modern technology. Aerodynamic heat, during reentry creates a number of interesting airframe bearing problems. Most of the airframe bearings are adequately insulated but there are critical areas where high-temperature lubrication is required. Modern jet engines require both high-temperature liquid and solid lubricants. Table 1 itemizes a number of current high technology areas where there is a critical need for high-temperature solid lubricants or self-lubricating bearing surfaces. Most of these applications are for engines such as the adiabatic diesel, the small gas turbine, or the rotary engine. These engine types are not new. What is relatively new is the accelerated trend toward higher temperatures in the most recent designs.

Two basic approaches to improving engine efficiency are 1) to employ the largest practicable ΔT in the theoretical thermodynamic cycle and 2) to minimize heat losses in the real engine. The first approach is motivated by a desire to improve the theoretical thermodynamic efficiency as expressed by the well-known Carnot equation:

$$\frac{W(max)}{q(in.)} = \frac{T(max) - T(min)}{T(max)} = \frac{\Delta T}{T(max)}$$

which states that the maximum quantity of work that can be extracted from a given quanitity of heat increases with ΔT in the thermodynamic cycle. Because of heat losses, no real engine efficiency approaches the theoretical maximum, but an increase in the Carnot efficiency improves the potential for

improved efficiency in real engines. The second and more feasible approach is to bring the real efficiency closer to the Carnot efficiency by reducing heat losses to the coolants and the exhaust. (It has been shown that an incredible 50 to 60 percent of the energy released by fuel combustion in a modern internal combustion engine is lost to the coolant and the exhaust (1). The relevancy of these observations to this symposium is obvious. To improve efficiency engines must run hotter. This of course imposes higher temperature requirements upon engine materials and critically so for lubricants and bearing materials. If we do not use high-temperature lubricants and bearing materials, they will have to be cooled and insulated. The resulting increase in weight and complexity could easily negate gains due to improving the thermal efficiency of the basic engine design. Therefore, there is current interest in solid lubrication for use at temperatures up to 1000° C and higher. At temperatures above about 300° C, we have difficulty finding layer-lattice compounds or organic polymers that are both oxidatively and thermally stable in air (2). We, therefore, need to creatively search for other classes of solid materials with desirable tribological properties.

HARD COATING MATERIALS

Oxidation temperatures and hardnesses (3) of some important carbides and nitrides are compared in Table 2. Coatings of all the compounds listed are hard enough to have good wear resistance, assuming adequate cohesion and bond to the substrate can be achieved. However, a considerable variation in oxidation resistance exists. Chromium carbide, boron carbide, silicon nitride, and silicon carbide are oxidatively stable to at least 1000° C while tungsten and titanium carbides oxidize during long-duration exposure to air at temperatures above about 540° C. Tungsten carbide tends to oxidize more rapidly than titanium carbide because its oxides are volatile at high temperature and their sublimation tends to accelerate the oxidation. Titanium nitride is another promising hard coat material, but it will convert to the oxide at about 550° C. However, some titanium carbide- and titanium nitride-sputtered coatings have shown surprisingly good resistance to oxide conversion at higher temperatures than listed in Table 2. Oxidation occurs, but the rate is very low, probably because of high-coating density and the passivating nature of the initially formed oxide films, which protects the coating against catastrophic oxidation.

Sputtered chromium oxide (Cr_2O_3) is an interesting antiwear coating. In start-stop tests, an optimized sputtered coating of Cr_2O_3 on nickel-chromium foil bearings has shown outstanding endurance over a wide temperature range (4). For example, the coating did not wear out after 9000 start-stop rubs against a journal coated with chromium carbide at temperatures from room ambient to 650° C.

Although some hard-coating materials have good wear resistance, they generally are not low-friction materials. When low friction is required in addition to wear resistance, some types of softer materials are of interest.

PLASTICITY AND SOLID LUBRICANTS

The problem is to determine what properties give a solid lubricating ability and then to find materials with those properties at elevated tem-

peratures. In previously reported research performed at NASA Lewis, the behavior of solid lubricants and abrasives on a microscopic level were observed and compared (5). Figure 1 shows the deformation characteristics of graphite fluoride (CF_x) in a Hertzian sliding contact. Similar photomicrographs of molybdenum disulfide (MoS_2) are shown in Fig. 2. A common characteristic of both solids is that they readily undergo plastic flow and look much like grease or paste within the contacts. The individual particles coalesce by plastic flow into a continuous film which adheres to the lubricated surfaces. Contrast this behavior with that of silicon carbide (SiC) shown in Fig. 3. Silicon carbide particles fracture and then abrade the surfaces as they pass through the contact.

Good adherance is also important for the lubrication of Hertzian contacts in order to ensure adequate traction for drawing the lubricant into the highly loaded contact; Fig. 4 (6), contrasts the behavior of oil-dispersed MoS_2 with the previously shown dry MoS_2 in the vicinity of a Hertzian contact. Apparently, the oil wets the sliding surfaces and, the MoS_2 particles; insufficient traction exists to draw the solid particles into the contact, which then accumulate at the inlet or are swept around it. From these observations, a qualitative model of solid lubricant behavior can be inferred. Requirements for solid lubrication in this proposed model are that the solid lubricant must have (a) a high degree of plasticity for easy shear, (b) the ability to coalesce its individual particles under load and shear to form continuous coherent films, and (c) the ability to adhere to the lubricated surfaces.

If we think in terms of easy plastic flow by any available mechanism (not restricting ourselves to the mechanism of basal plane slip in layer-lattice compounds), we can broaden tremendously the scope of materials considered as possible solid lubricants. We can further broaden the scope by considering the visco-plastic flow of glazes on crystalline solids containing a glassy (vitreous) phase and the viscous flow of completely vitreous glazes. Any of these flow mechanisms can provide lubrication if the shear strengths of the films are low enough, and adherance to the lubricated surface is adequate.

FLUORIDE-METAL COMPOSITES

Calcium fluoride (CaF_2) is a good example of a compound which is non-lubricative in the brittle condition at low temperatures but becomes lubricative above 500° C when it undergoes a transition from a brittle to plastic state.

Calcium fluoride has been used in a number of high-temperature applications primarily as a component of self-lubricating composites. Table 3 gives examples of some components in high-temperature, self-lubricating composites. The metal matrix material is employed to obtain machinability, thermal shock resistance, and a thermal expansion coefficient match with nickel-base superalloys. The thermal expansion match is essential to obtain adequate bonding when the composites are applied as coatings on nickel-alloy substrates. Hard oxides are sometimes used to improve hardness and wear resistance. Thermally stable fluorides such as CaF_2 and barium fluoride (BaF_2) function as high-temperature solid lubricants. Finally, glass is added to some composites to function as an oxygen barrier and thereby provide a degree of oxidation protection to the metal components of the composite.

Some preparation methods and important characteristics of composites for tribological applications are shown in Table 4. Plasma (thermal) spraying in recent years has been a relatively convenient way to prepare composite coatings. Multicomponent powders can be codeposited without excessive heating of the substrate, and there is no need for presses and dies. Coatings can be applied by a handheld plasma-spray torch. More sophisticated installations incorporate automated spray equipment but the basic principle is the same. The plasma-spray process consists of transporting powders of the coating components with a carrier gas through a very high-temperature, high-energy arc containing ionized gas, usually argon. The particles in their passage through this plasma of argon are melted. They impinge on the material to be coated and adhere by a combination of mechanical and diffusion bonding. An excess coating thickness is applied and then machined back to the desired thickness. This machining operation is not required for some applications of plasma-spray coatings, but is necessary for bearing applications because close tolerances and a smooth surface finish are required.

Figure 5 illustrates the microstructure of a polished composite coating applied by plasma spraying. This coating contains nichrome, silver, and CaF_2. It is essential to achieve a uniform distribution of components, especially when the bearing contact areas are small as in nominal point and line contacts. If the distribution is not uniform, there is no assurance that the area in actual sliding contact is representative of the coating's average composition, and friction and wear properties will be erratic.

Two plasma-sprayed coating compositions were successfully employed in the space shuttle and in the hot section of small jet engines. The coatings are designated as PS100 and PS101 whose compositions by weight are 67 nichrome, 16.5 CaF_2, 16.5 glass and 30 nichrome, 30 Ag, 25CaF_2, 15 glass, respectively. The glass is a special sodium-free composition to minimize oxygen diffusion. Its composition is 58 SiO_2, 21 BaO, 8 CaO, 13 K_2O.

Figure 6 (2) gives the friction coefficient of PS100 and PS101 coatings from room temperature to about 900° C (1650° F). The upper curve with the very high friction coefficient is for a plain spherical bearing of nickel chromium alloy with no coating. (The alloy was, however, preoxidized to reduce adhesion of the sliding surfaces.) The friction coefficient was quite high over the entire temperature range, and the bearing seized at about 850° C. The coating that contained nichrome, CaF_2, and glass provided good lubrication from about 500° to 900° C, but was unsatisfactory at lower temperatures. By adding silver to the composite, a reasonably low friction was obtained over the entire temperature range.

The friction and wear data for PS101 in moderate vacuum, cold nitrogen gas, and in air are summarized in Table 5. The lowest friction was observed in the 5×10^{-2} torr vacuum where the friction coefficient was 0.15. Wear rates tended to decrease with test duration. Total diametral bearing wear was 4.5×10^{-3} cm after 5000 oscillating cycles at a unit load of 35 MPa (5000 psi). In cold nitrogen (-107° C), friction coefficients were typically 0.22 and diametral wear after 5000 journal oscillations was 3.8×10^{-3} cm. As previously discussed, friction coefficients in air from room temperature to 870° C were approximately 0.2 over the entire temperature range. Wear rates also were uniformly low over the entire temperature spectrum. These results clearly demonstrate the versatility of PS101 for lubricating plain journal bearings over an exceptionally wide range of temperatures and atmospheric conditions.

Figure 7 is a photograph of a PS100 application. In this case the coating was used as an interstage seal material between the compressor and turbine in a small jet engine, with the seal operating at 650° C (1200° F). The main shaft of the engine rotated in the seal. The shaft had six knife edges that rubbed against the coating material. Previously, an abradable porous material was used in this seal, but the erosion rate was very high, and there was considerable gas leakage through the pores of the abradable material. The nichrome, CaF_2, and glass were then plasma sprayed as a top coat over the abradable material. Because this coating was nongalling, the knife edges cut through it cleanly without exccessive material transfer. Because the coating was dense, erosion resistance improved, and there was considerable reduction in gas leakage through the seal.

FLUORIDE-OXIDE COMPOSITE COATINGS

Because of the limitations imposed by oxidation of metal matrix coatings, completely nonmetallic coatings are of interest. It has been reported that plasma-sprayed coatings of nickel oxide containing about 15 percent CaF_2 have good high-temperature wear resistance (8). This coating is plasma-sprayed onto seal bars for regenerators used in automotive gas-turbine engines to improve thermal efficiency. The coatings must be wear resistant at high tempertures while in sliding contact with a porous ceramic regenerator core. The core material is generally lithium-aluminum silicate (LAS), magnesium-aluminum silicate (MAS), or aluminum silicate (AS).

Current preliminary research at NASA Lewis has shown that plasma-sprayed coatings based on zirconium oxide and CaF_2 have excellent thermal stability in addition to attractive tribological properties. Figure 8 gives the friction and wear coefficients of plasma-sprayed coatings of ZrO_2-CaF_2 with and without silver additions. In these experiments, the coating was on the cylindrical surface of a rotating disk and placed in sliding contact with two flat nickel base superalloy rub blocks. Both coating combinations had fairly high wear rates at room temperature, but wear rates were much lower for the ZrO_2 - CaF_2 coating at 650° C. Silver additions were detrimental and did not have the beneficial effect of improving room temperature friction and wear that it had on the metal matrix composites. Wear of the uncoated metal specimens that slid against the coatings was low in all cases indicating that the coatings were not abrasive to the metal rub shoes. Friction coefficients were 0.40 at room temperature and 0.22 + 0.04 at 650° C for the ZrO_2 - CaF_2 coating. Higher temperature experiments will demonstrate whether these coatings have a maximum temperature advantage over the metal matrix composites.

CONCLUDING REMARKS

For wear control, hard materials such as some selected carbides, nitrides, and oxides are serviceable to 1000° C. Some soft fluorides provide lubrication above their brittle-to-ductile transition temperaures to as high as 900° C. They are currently used as the lubricating components of metal matrix composites. These composites are prepared by powder metallurgy methods such as hot pressing and sintering or by plasma-arc spraying. At even higher temperatures, nonmetallic compositions are of interest.

REFERENCES

1. Pinkus, O. and Wilcock, D. F., eds., Strategy for Energy Conservation Through Tribology, ASME, New York, 1977.
2. Sliney, H. E., "High Temperature Solid Lubricants: Part 1: Layer Lattice Compounds and Graphite," Mechanical Engineering, Vol. 96, No. 2, Feb. 1974, pp. 18-22.
3. Lynch, J. F., Ruderer, C. G., and Duckworth, W. H., eds., Engineering Properties of Selected Ceramic Materials, American Ceramic Society, Columbus, OH, 1966.
4. Bhushan, B. and Gray S., "Development of Surface Coatings for Air-Lubricated, Compliant Journal Bearings to 650° C, ASLE Transactions, Vol. 23, No. 2, Apr. 1980, pp. 185-196.
5. Sliney, H. E., "Dynamics of Solid Lubrication as Observed by Optical Microscopy," ASLE Transactions, Vol. 21, No. 2, Apr. 1978, pp. 109-117.
6. Cusano, C. and Sliney, H. E., "Dynamics of Solid Dispersions in Oil During the Lubrication of Point Contact, Part II - Molybdenum Disulfide," ASLE Transactions, Vol. 25, No. 2, Apr. 1982, pp. 190-197.
7. Sliney, H. E., "Wide Temperature Spectrum, Self-Lubricating Coatings Prepared by Plasma Spraying," Thin Solid Films, Vol. 64, 1979, pp. 211-217.
8. Moore, G. D. and Ritter, J. E., "The Friction and Wear Characteristics of Plasma-Sprayed NiO-CaF_2 in Rubbing Contact with a Ceramic Matrix," Lubrication Engineering, Vol. 30, No. 12, Dec. 1974, pp. 596-604.

TABLE 1. - WHY HIGH-TEMPERATURE SOLID LUBRICANTS?

Application	Temperature, °C
• Adiabatic diesel cylinder liner	600 - 1100
• Automotive gas turbine engine:	
Regenerator wear face	260 - 1100
Foil bearing (main shaft)	650
• Rotary engine for general aviation	
Apex seals	300 - 650
• Aircraft G.T.E.	
Variable stator vane (compressor, current)	350
Bushings (turbine, near future)	1000
Thrust reversal bearings	800
• Supersonic aircraft	
Control surface bearings	350
Control surface rub seals	650
• Shuttle	
Control surface rub seals	850

TABLE 2. - BULK PROPERTIES OF SOME HARD COAT MATERIALS[a]

Material	Microhardness, kg/mm^2	Oxidation temperature[b], °C
B_4C	4200	1090
TiC	3200	540
SiC	2900	1650
Cr_3C4	2650	1370
WC	2050	540
Si_3N4	2000	1400
TiN	1950	540
Cr_2O3	[c]1800	----

[a]Data from: Engineering Properties of Ceramic Materials, Battelle Memorial Institute. Published by American Ceramic Society, Columbus Ohio, 1966.
[b]Temperature for appreciable detrimental oxidation (passivating oxide films form at lower temperatures).
[c]Estimated conversion from published Moh hardness of 9.

TABLE 3. - INORGANIC COMPOSITES COMPONENTS AND THEIR FUNCTION

Metals	
	Ductility machinability
	Bonding thermal shock resistance
Oxides (ceramics)	
	Hardness, oxidation resistance, wear resistance
Thermally stable salts	
	High temperature lubrication (>500° C)
Glass	
	Oxidation-protection of metal
	Glaze former on wear surface

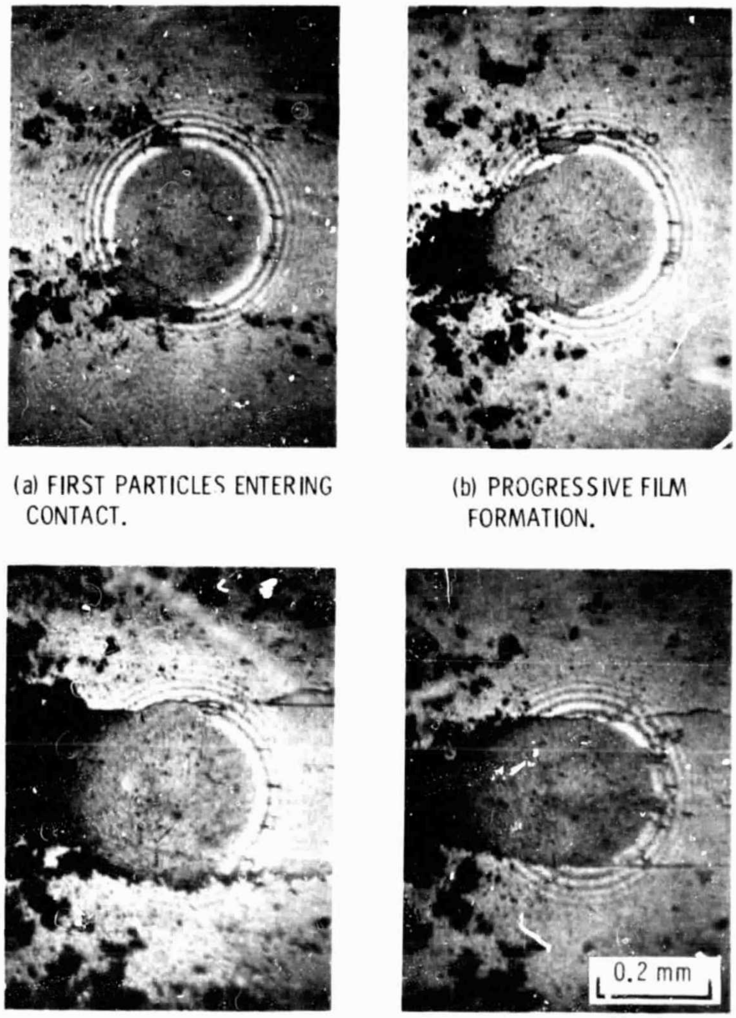
TABLE 4. - INORGANIC COMPOSITES

Preparation
Hot pressing
Cold press-sinter-infiltrate
Plasma spray
Important characteristics
Low friction and wear
Chemical and dimensional stability
Develops smooth wear surfaces
Wear particle type and dynamics (interacts with bearing design)

TABLE 5. - PERFORMANCE SUMMARY FOR OSCILLATING PLAIN SLIDING BEARINGS SELF-LUBRICATED WITH A PLASMA-SPRAYED COATING IN VARIOUS ATMOSPHERES

[PS101 Coating: 30 Ag, 30 NiCr, 25 CaF_2, 15 glass; 0.025 cm (0.010 in.) thick; 3.5×10^7 N/m^2 (5000 psi) unit load, ±15° oscillation at 1 hertz.]

Bearing temperature		Ambient atmosphere	Typical friction coefficient	Increase in radial clearance	
				$cm\times10^3$ (milliinches)	
°C	°F			After 100 cycles	After 5000 cycles
Room	Room	Vacuum 5×10^{-2} torr	0.15	1.3 (0.5)	4.5 (1.8)
-107	-160	Nitrogen	.22	0.3 (0.1)	3.8 (1.5)
Room	Room	Air 760 torr	.24	.5 (0.2)	7.0 (2.8)
540	1000	↓	.19	.5 (0.2)	6.0 (2.4)
650	1200	↓	.21	.3 (0.1)	2.5 (1.0)
870	1600	↓	.23	.3 (0.1)	2.5 (1.0)



(a) FIRST PARTICLES ENTERING CONTACT.

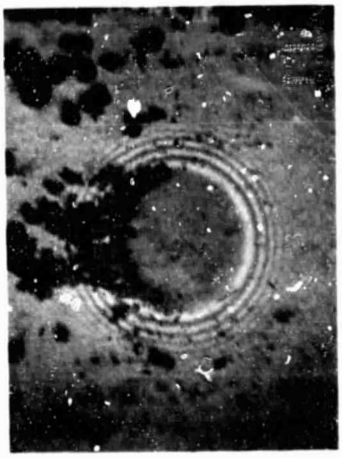
(b) PROGRESSIVE FILM FORMATION.

(c) PROGRESSIVE FILM FORMATION.

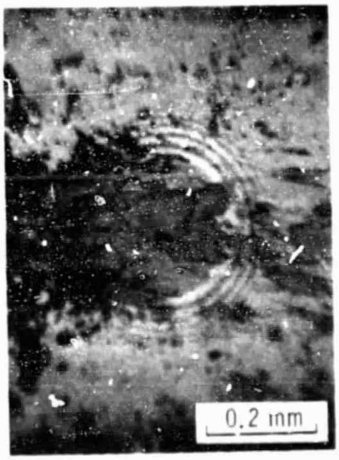
(d) COMPLETE FILM FORMATION AFTER ONLY 10 mm OF SLIDING.

Figure 1. - Behavior of graphite fluoride in initially unlubricated contact. Load, 13.2 N (3 lb); original magnification, X150.

(a) LUBRICANT PARTICLES APPROACHING CONTACT.



(b) PARTICLES ENTERING CONTACT.



(c) EXTENSIVE PLASTIC FLOW OF MoS_2 IN CONTACT.

Figure 2. - Behavior of MoS_2 powder in an initially unlubricated contact, 13.2 N (3 lb) load. Original magnification, X150.

(a) SiC PARTICLE ENTERING CONTACT.

(b) PARTICLE PART WAY THROUGH CONTACT.

(c) PARTICLE AT CONTACT EXIT.

(d) CONTACT AFTER 10 DISK REVOLUTIONS.

Figure 3. - Abrasive action of silicon carbide particles. Load, 13.2 N (3 lb); original magnification, X150.

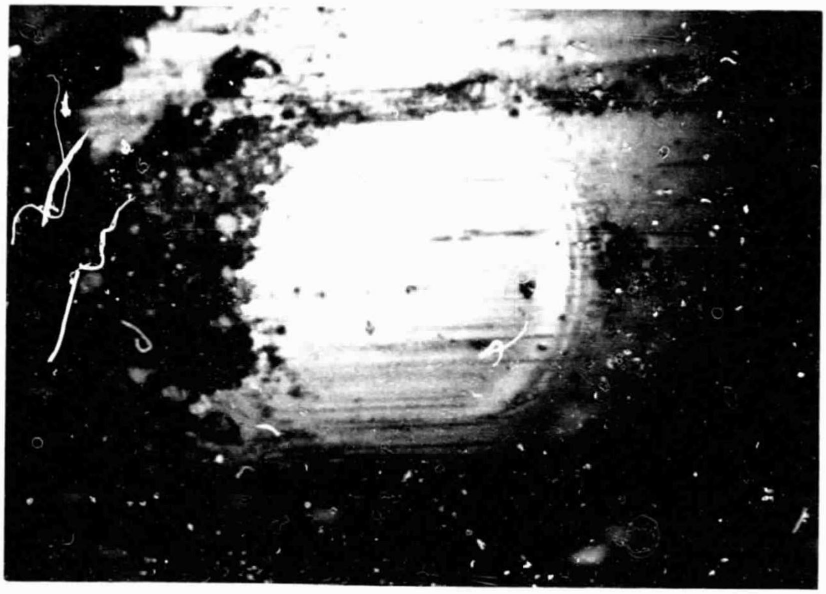


Figure 4. - Solid lubricant pile-up at inlet of sliding contact. Lubricant is a 0.5% dispersion of MoS_2 in 150 cS mineraloil.

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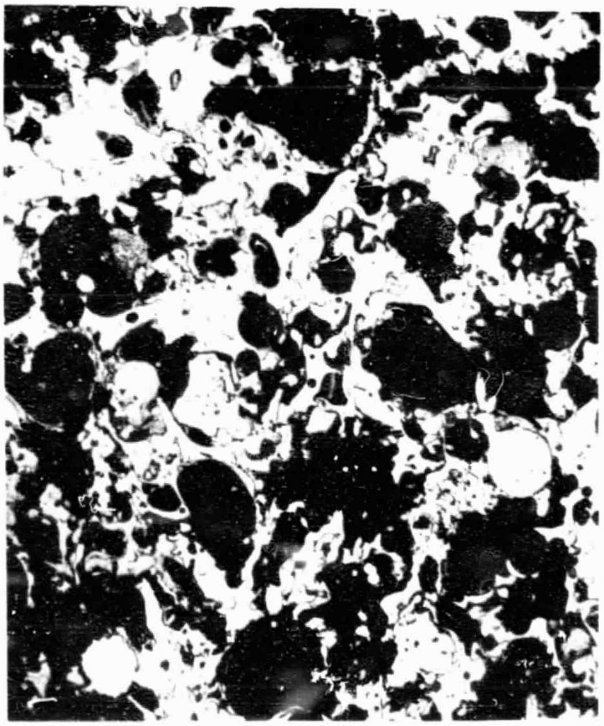

ORIGINAL MAGNIFICATION, X100

Figure 5. - Microstructure of plasma sprayed composite.

200 μm

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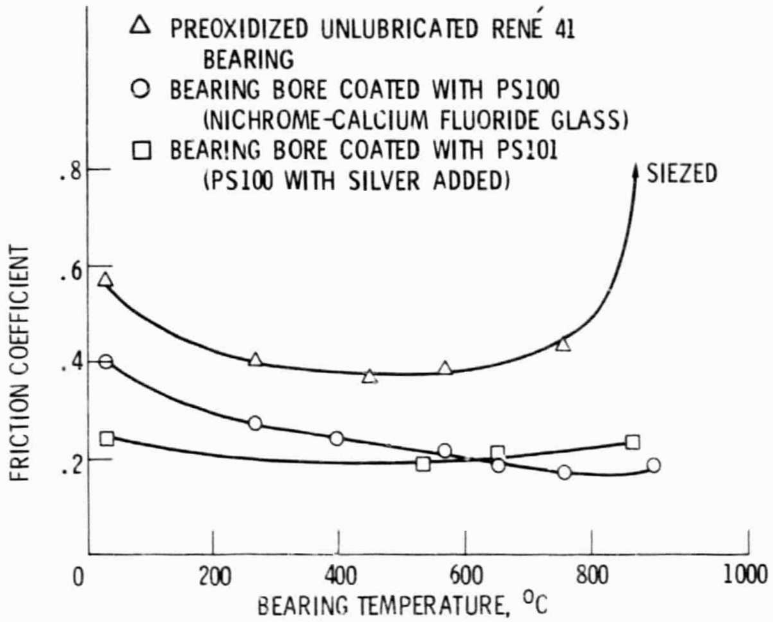

Figure 6. - Bearing friction.

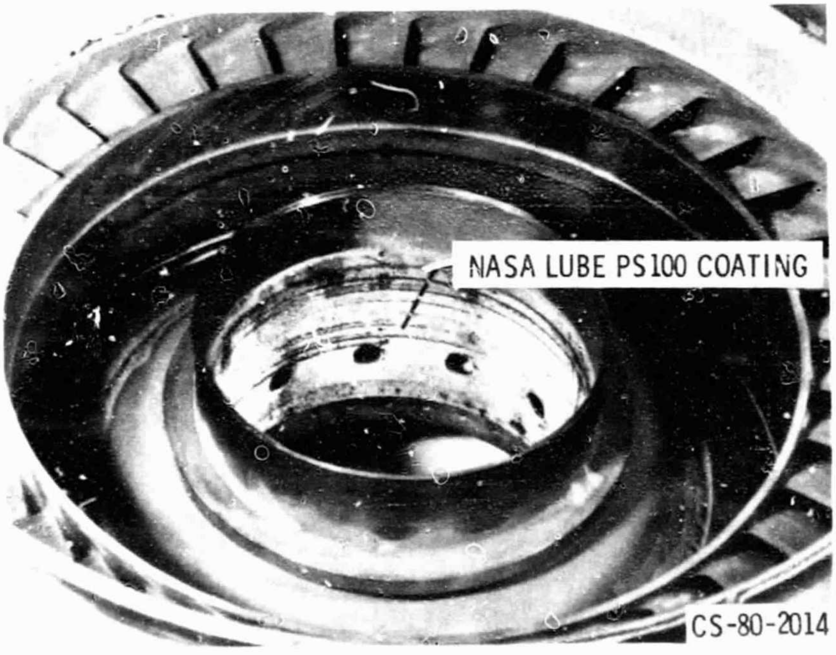

Figure 7. - Compressor/turbine shaft seal-operates at 650° C.

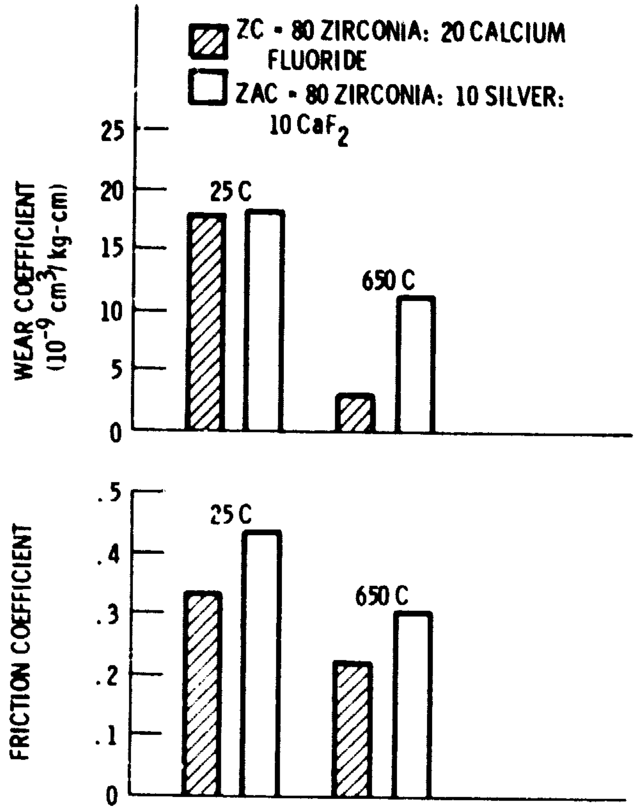

Figure 8. - Wear and friction of plasma-sprayed coatings of zirconia and calcium fluoride, with and without silver. Double rub shoe tests with 22.7 kg per Inconel shoe against coated disk at 0.3 m/sec (150 rpm).